

Algorithms for Exact Counting of Energy Levels of Spectroscopic Transitions at Different Temperatures

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ABSTRACT: The KDB energy level counting algorithm [M. J. H. Kemper, J. M. F. Van Dijk, and H. M. Buck, *Chem. Phys. Lett.*, **53**, 21 (1978)] has been modified such as to generate simultaneously the internal energy levels in two different states. Such algorithms are necessary for a description of the temperature dependence of the rotovibronic fine structure of electronic transitions as well as the rotatory fine structure of vibrational spectra. The performance of two versions of the algorithms as well as extensions to restrict the generation scheme to selected modes are discussed. © 1997 by John Wiley & Sons, Inc. *J Comput Chem* **18**: 1312–1319, 1997

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Introduction

The exact enumeration of internal molecular energy levels plays an important role in the determination of the density of states as well as in the quantum-chemical simulation of the fine structure of molecular spectra. Because, in the statistical theory calculations of rate constants for unimolecular reactions and nonradiative relaxation processes are based on the density of states,^{1–4} several methods have been proposed for the evaluation of

this quantity. Classical and semiclassical approximations^{5,6} and their semiempirical extensions^{7,8} yield estimates of the density of states, whereas counting algorithms generate all energy levels in a given interval. Beyer and Swinehart (BS) developed such an algorithm,⁹ which has been modified to include anharmonic effects by Stein and Rabinovitch,¹⁰ and extended by Quack^{11,12} and later by Sinha and Kinsey¹³ for the determination of the number of states that belong to each irreducible representation of the point group under consideration.

The disadvantage of the BS method and its extensions is that they do not show precisely what states (as characterized by their quantum num-

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bers) lie in a certain region. This information, which is a necessary prerequisite for an evaluation of the intensities of molecular spectra, can be obtained from the backtracking procedure proposed by Kemper, van Dijk, and Buck (KDB).¹⁴ The KDB algorithm (as well as the BS algorithm) implicitly assumes that, for a spectroscopic transition, all vibrational and/or rotational quantum numbers of the initial state are zero. But “hot bands” are common features in room temperature spectra, and therefore a realistic simulation of the fine structure of molecular spectra requires a consideration of nonzero vibrational and/or rotational quantum numbers of the initial state. No counting algorithm for this task has been reported so far.

In this study we present two modifications of the KDB algorithm that make it possible to evaluate all combinations of quantum numbers of the initial and the final state that correspond to energy differences which fall into a certain interval. Thus, total intensities of the complete spectrum at a given temperature can be obtained by dividing the spectrum into intervals $x_i \pm \Delta x$ according to the desired resolution¹⁵ and successively calculating the intensity for each interval, taking into account the population of the various levels of the initial state at this temperature. Applications to room temperature absorption and emission spectra of benzene and diazabenzenes as well as to the hot band structure of the chemiluminescence spectrum of the HSO radical clearly show that the algorithms are necessary to simulate vibronic fine structures and to support the assignment of individual hot bands.^{16,17}

Backtracking Procedure

The aim of the backtracking KDB algorithm is to enumerate all possible combinations of quantum numbers $\vec{v}' = (v'_1, \dots, v'_N)$ of the vibrational and rotational degrees of freedom (collectively referred to as modes) of the final state for which the corresponding energy, $E_{v'_1, \dots, v'_N}$ relative to the $0 \rightarrow 0$ transition energy, falls into a given energy interval, $x_i \pm \Delta x$. Starting with $j = 1$, this is achieved by scanning v'_j and testing the corresponding energies. If the energy is higher than the upper limit of the interval, one sets $v'_j = v'_j - 1$ and v'_{j+1} is scanned in the same way, until for $j = N$ the energy is too high. In this case, one sets $v'_k = v'_k - 1$, where k is the largest integer smaller than j for which $v'_k \neq 0$, and the procedure is started again with $j = k + 1$ and $v'_l = 0$ for all $l > k$.

This is illustrated in Figure 1, using, as an example, two states of a hypothetical harmonic system with two vibrational degrees of freedom with normal coordinates Q_1 and Q_2 and vibrational wave numbers, $\omega_1 = 100 \text{ cm}^{-1}$, $\omega_2 = 120 \text{ cm}^{-1}$ of the initial state and $\omega'_1 = 70 \text{ cm}^{-1}$, $\omega'_2 = 90 \text{ cm}^{-1}$ of the final state. Potential energy surfaces are shown in Figure 1a and values of the quantum numbers v_i and v'_i are given in Figure 1b, whereas, in Figure 1c, transitions from the vibrationless initial state into various levels of the final state are indicated by full arrows. Hot vibrational bands, which are generated only by the modified algorithms, are also shown; they are drawn as broken arrows. The resulting spectrum is plotted in Figure 1d assuming arbitrary intensities. For the interval $0 \text{ cm}^{-1} \leq E < 100 \text{ cm}^{-1}$, where E is the energy relative to the $0 \rightarrow 0$ transition, the KDB algorithm yields the states $\vec{v}' = (1, 0)$ and $\vec{v}' = (0, 1)$, whereas for $100 \text{ cm}^{-1} \leq E < 200 \text{ cm}^{-1}$ the states $(2, 0)$, $(1, 1)$, $(0, 2)$ are obtained in this order. The spectrum can be calculated by evaluating the intensity for each of these transitions. In practical calculations, for systems with many energy levels, the interval $x_i \pm \Delta x$ is chosen according to the desired resolution of the spectrum (e.g., 5 cm^{-1}), all intensities within one interval are added and the various intervals $x_i \pm \Delta x$ are calculated to produce the desired spectrum.

Note that the KDB algorithm produces all levels except the $0 \rightarrow 0$ transition. Therefore, the $0 \rightarrow 0$ transition has to be explicitly taken care of in the enumeration of energy levels and the evaluation of intensities, as in the case of the two modifications of the KDB algorithm described in the following two sections.

Both modifications generate, for each spectral interval $x_i \pm \Delta x$, all combinations of quantum numbers that are connected to an initial level \vec{v} with a population probability $W(\vec{v})$ greater than a predetermined value S . In this way, only those combinations are generated which may yield a significant contribution to the spectrum. Assuming a Boltzmann distribution, the minimal population of the initial state at a given temperature that has to be considered can also be characterized by an energy V_{\max} , which the system can have in its initial state.

Interlocked Algorithm

We first describe a modification of the KDB algorithm to take into account nonzero quantum

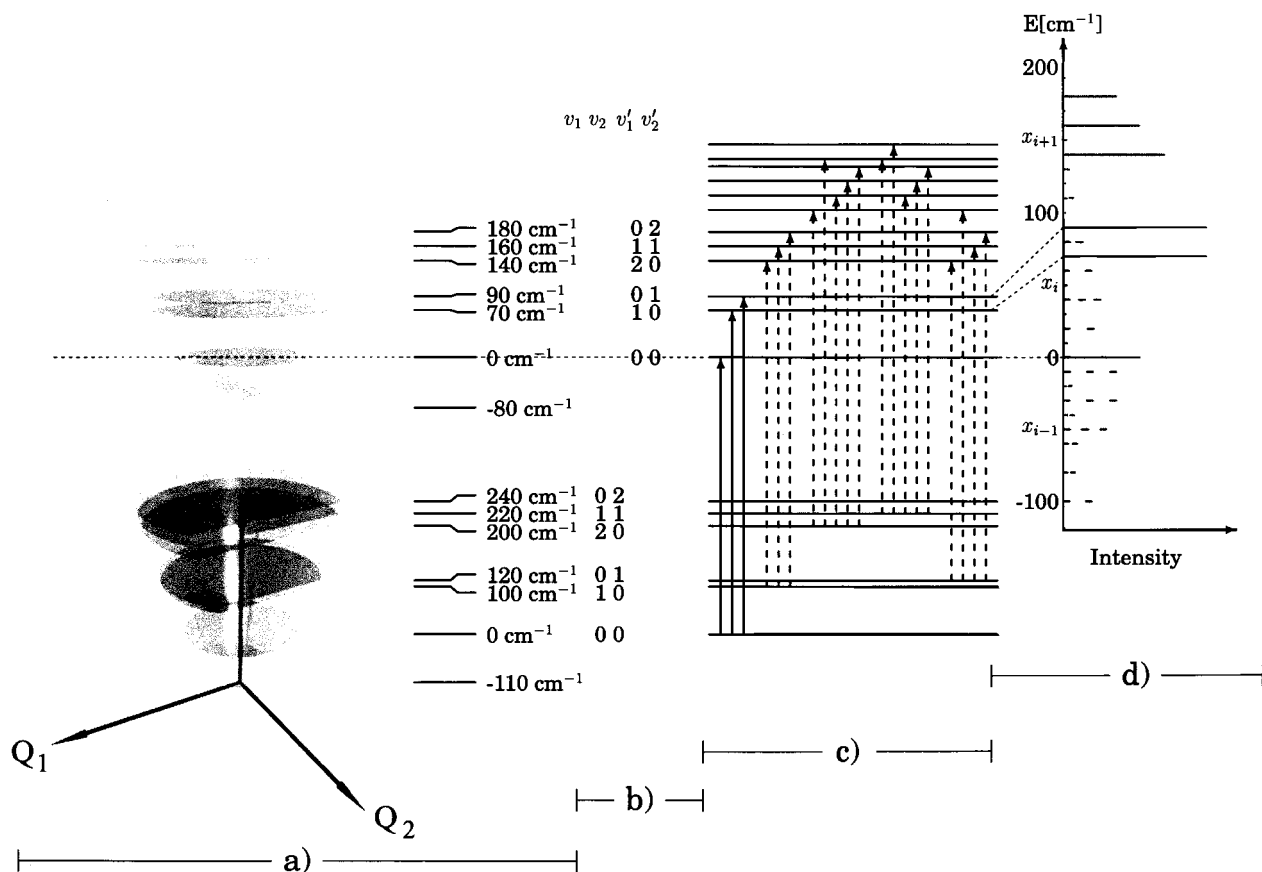


FIGURE 1. Illustration of the algorithms (see text). (a) Potential energy surfaces; (b) vibrational quantum numbers; (c) generated transitions; (d) resulting spectrum.

numbers of the initial state that consists of two interlocked KDB procedures; an *outer loop* generates all combinations \vec{v} with energies V not greater than V_{\max} , whereas an *inner loop* [steps (3)–(7)] generates, for each of these \vec{v} , all possible combinations of quantum numbers \vec{v}' of the final state that yield transition energies E , which fall into the given interval $x_i \pm \Delta x$. Note that, in contrast to the original KDB procedure, $\vec{v} = (0, \dots, 0)$ and $\vec{v}' = (0, \dots, 0)$ are generated explicitly.

In principle the algorithm works as follows: For a system with N modes, two arrays N_j and F_j , $j = 1, \dots, 2N$ are initialized. The first N elements are used for the quantum numbers v_i and wave numbers ω_i of the initial state and the second N elements for v'_i and ω'_i of the final state (necessarily, all $\omega_i > 0$ and all $\omega'_i > 0$). The total internal energy with respect to the $0 \rightarrow 0$ transition, the internal energy of the initial state, and the intensity are given by the variables E , V , and I , respectively. The region of the spectrum to be calculated is divided into intervals x_i of a given width $2\Delta x$.

For each interval $x_i \pm \Delta x$ we execute the following statements:

- (1) Set $F_j = \omega_j$ ($j = 1, \dots, N$) or ω'_{j-N} ($j = N + 1, \dots, 2N$), set E , V , I and all N_j to the initial value of zero, and start with $j = 1$, set $Z_1 = 1$, where Z_1 is a switch necessary to generate $\vec{v} = (0, \dots, 0)$;
- (2) If $Z_1 = 1$, set $Z_1 = 0$ and go to (3), set $N_j = N_j + 1$ and $V = V + F_j$, if $V > V_{\max}$ go to (9);
- (3) Set $N_k = 0$ for $N < k \leq 2N$ and set $E = -V$, set $l = N + 1$, where $l = N + 1, \dots, 2N$ labels the modes of the final state, set $Z_2 = 1$, where Z_2 is needed to generate $\vec{v}' = (0, \dots, 0)$;
- (4) If $Z_2 = 1$, set $Z_2 = 0$ and go to (5), set $N_l = N_l + 1$, $E = E + F_l$ and $Z_2 = 2$;
- (5) If $E < x_i - \Delta x$, go to (4), if $x_i - \Delta x \leq E < x_i + \Delta x$, calculate I and go to (4);

- (6) If $Z_2 = 0$, go to (8),
set $N_l = N_l - 1$, $E = E - F_l$;
- (7) If $L < 2N$, set $l = l + 1$ and go to (4),
start with $k = 2N - 1$ and while $N_k = 0$,
set $k = k - 1$,
if no $k > N$ with $N_k > 0$ exists, go to (8),
or else set $N_k = N_k - 1$ and $E = E - F_k$,
set $l = k + 1$,
for all $k \geq l$ set $N_k = 0$ and correct E
accordingly, go to (4);
- (8) If $V \leq V_{\max}$ go to (2);
- (9) Set $N_j = N_j - 1$ and $V = V - F_j$,
if $j \neq N$, set $j = j + 1$ and go to (2),
start with $k = N - 1$ and while $N_k = 0$, set
 $k = k - 1$,
if no $k > 0$ with $N_k > 0$ exists, go to (10),
set $N_k = N_k - 1$ and $V = V - F_k$,
set $j = k + 1$,
for all $k \geq j$ and $k \leq N$ set $N_k = 0$, correct V
accordingly and go to (2);
- (10) Print I

Taking $V_{\max} = 230 \text{ cm}^{-1}$ the algorithm generates, for the interval $0 \leq E < 100 \text{ cm}^{-1}$, the following combinations of quantum numbers (v_1, v_2, v'_1, v'_2) : (0, 0, 0, 0), (0, 0, 1, 0), (0, 0, 0, 1) and (1, 0, 2, 0), (1, 0, 1, 1), (1, 0, 0, 2), (2, 0, 3, 0), (2, 0, 4, 0), (2, 0, 2, 1), (2, 0, 1, 2), (2, 0, 0, 3), (1, 1, 4, 0), (1, 1, 3, 1), (1, 1, 2, 1), (1, 1, 1, 2), (1, 1, 0, 3), (0, 1, 2, 0), (0, 1, 3, 0), (0, 1, 1, 1), (0, 1, 0, 2). All except the first three combinations correspond to hot bands and are indicated in Figure 1d by broken lines. To evaluate the spectrum, the intensities of these hot bands have to be multiplied with the occupation probability $W(\vec{v})$ of the initial state. Due to the wave numbers chosen in the example, some of the hot bands coincide and only a few of them are assumed to show a noticeable intensity as indicated in Figure 1d.

Extended Algorithm

Next we describe an alternative modification of the KDB algorithm that generates all necessary combinations of \vec{v} and \vec{v}' in *one*, rather than in *two* loops as in the interlocked version. Furthermore, instead of starting with $\vec{v} = \vec{0}$, for each mode j of the initial state the highest possible v_j consistent with V_{\max} is determined and used as the initial value in \vec{v} .

Now we can scan all those modes as described for the KDB algorithm via stepping *up* the quan-

tum numbers of the final state and stepping *down* the quantum numbers of the initial state until $v_j = 0$ is reached.

The detailed steps are as follows: In addition to E , V , and I and the arrays N_j and F_j , which have the same meaning as before, an array A_j is initialized with $A_j = 0$ for all modes of the final state, whereas for the modes of the initial state A_j equals the largest integer consistent with $A_j F_j \leq V_{\max}$. After dividing the spectrum into intervals $x_i \pm \Delta x$ execute the following statements:

- (1) Start with all $N_j = A_j$, set $E = -\sum_{j=1}^{2N} A_j F_j$, $V = -E$ and $j = 1$,
- (2) If j denotes a mode of the final state, set $N_j = N_j + 1$, or else set $N_j = N_j - 1$ and $V = V - F_j$,
If $N_j < 0$, go to (4),
set $E = E + F_j$;
- (3) If $E < x_i - \Delta x$, go to (2),
if $E \geq x_i + \Delta x$, go to (4),
if $V \leq V_{\max}$, calculate I ,
go to (2);
- (4) If j denotes a mode of the final state, set $N_j = N_j - 1$, or else set $N_j = N_j + 1$ and $V = V + F_j$,
set $E = E - F_j$;
- (5) If $j < 2N$, set $j = j + 1$ until j denotes a mode of the final state or $A_j \neq 0$ or $j = 2N$,
if $j < 2N$, go to (2);
- (6) Start with $k = 2N - 1$ and while $N_k = A_k$,
set $k = k - 1$,
if no $k > 0$ with $N_k \neq A_k$ exists, go to (7),
if k denotes a mode of the final state, set $N_k = N_k - 1$, or else set $N_k = N_k + 1$ and $V = V + F_k$,
set $E = E - F_k$, $j = k + 1$,
for all $k \geq j$ set $N_k = A_k$ and correct E and V correspondingly,
go to (2);
- (7) Print I

Using $j = 1, 2$ for the initial state and $j = 3, 4$ for the final state, the extended algorithm generates, in our example, the same combinations of quantum numbers, but in different order.

Taking $V_{\max} = 230 \text{ cm}^{-1}$ we obtain, for $0 \leq E < 100 \text{ cm}^{-1}$, a starting vector $\vec{A} = (2, 1, 0, 0)$ and the following combinations of quantum numbers: (0, 0, 0, 0), (0, 0, 1, 0), (0, 0, 0, 1) and (0, 1, 2, 0), (0, 1, 3, 0), (0, 1, 1, 1), (0, 1, 0, 2), (1, 0, 2, 0), (1, 0, 1, 1), (1, 0, 0, 2), (1, 1, 4, 0), (1, 1, 3, 1), (1, 1, 2, 1), (1, 1, 1, 2), (1, 1, 0, 3), (2, 0, 3, 0), (2, 0, 4, 0), (2, 0, 2, 1), (2, 0, 1, 2), (2, 0, 0, 3).

Note that although the starting vector \vec{A} itself may be consistent with V_{\max} and yields a transition energy falling in one of the $x_i \pm \Delta x$'s, the extended algorithm will not generate this transition, so it has to be added explicitly.

Performance

Both modifications of the KDB algorithm produce the same results, but they differ in performance and in the fields of application. Generally, the interlocked algorithm is faster, because, especially at higher temperatures, the extended algorithm generates many combinations of quantum numbers, which are later to be removed due to the low occupation probability of the initial state involved.

The extended algorithm, however, is much more convenient to use if specific modes of the initial state are to be excluded from the generation scheme; for instance, if from previous calculations it is known that certain modes do not contribute significantly to the spectrum. This can be done by simply setting $A_j = 0$ for these modes. In the same way, the maximum excitation levels of individual degrees of freedom can be reduced, which may be advantageous for low frequency modes at higher temperatures.

The performance of the algorithms depends on the ordering of the modes of the initial and the final state. While the interlocked algorithm requires the first and the second N elements N_j ($j = 1, \dots, N$ and $j = N + 1, \dots, 2N$) to contain the quantum number v_i of the initial state and v'_i of the final state, respectively, any order of the v_i and v'_i is possible for the extended algorithm. Except for some exotic cases, however, it is strongly recommended to first have all modes of the initial state in descending-frequency order and then the modes of the final state in the same order (cf.

Table V). The same ordering makes it possible to skip the generation of all combinations of quantum numbers \vec{v}' for a given \vec{v} , if it is already known that the corresponding $V(\vec{v})$ is greater than V_{\max} . This slight modification¹⁸ improves the performance of the extended algorithm such that, at intermediate temperatures, it is comparable to that of the interlocked algorithm. At higher temperatures, however, the latter will be faster.

To illustrate the previous statements we present here the results of some benchmark calculations for an example with 48 vibrational degrees of freedom, which may be viewed as a model system for naphthalene. Note that the total CPU times (IBM RS/6000 590) shown in Table V are only estimates of the performance of the *algorithm*, because the CPU time also reflects the efficiency of the *implementation*.

For all our calculations, we have used the parameters given in Table I and the wave numbers of the initial and final state given in Tables II and III, respectively. Table IV shows the number of generated transitions at various temperatures. Table V shows the total CPU times needed to calculate the combinations of the quantum numbers with different algorithms at various temperatures using modes in ascending and descending frequency order. In Figure 2, we have plotted the CPU times versus the temperature.

Obviously, only at very low temperatures do all algorithms lead to similar CPU times. At higher temperatures the unmodified extended algorithm becomes very inefficient. The modification improves the performance and extends the area of application. At higher temperatures, only the interlocked algorithm is sufficiently efficient, except for those cases in which the restriction of the excitation scheme provided by the extended algorithm may be used.

But even the CPU times for the interlocked algorithm increase exponentially with increasing temperature. Although this is not very encourag-

TABLE I.
Parameters for Naphthalene.

Normal modes	48
Wave number interval	– 1000 – 3000 cm ⁻¹
Width of intervals 2Δx	100 cm ⁻¹
Distribution	Boltzmann
Temperatures	0 K, 40 K, 60 K, 80 K, 100 K, 120 K, 140 K, 160 K, 180 K
Tolerance (S)	10 ⁻⁴ , 10 ⁻⁴ , 10 ⁻⁴ , 10 ⁻⁴ , 10 ⁻⁴ , 10 ⁻⁴ , 10 ⁻⁴ , 10 ⁻⁴
≜ V _{max} [cm ⁻¹]	0, 256.1, 384.1, 512.1, 640.1, 768.2, 896.2, 1024.2, 1152.3

TABLE II.
Wave Numbers of the Normal Modes of the Initial State [cm⁻¹].

3439	3438	3430	3430	3422	3420
3420	3419	1763	1729	1695	1650
1560	1540	1512	1437	1436	1352
1312	1260	1254	1252	1244	1238
1196	1172	1140	1081	990	982
957	914	906	900	901	863
804	797	631	582	520	517
498	496	425	387	173	168

TABLE III.
Wave Numbers of the Normal Modes of the Final State [cm⁻¹].

3439	3437	3427	3425	3421	3420
3419	3417	1805	1790	1714	1602
1523	1516	1494	1447	1407	1329
1329	1300	1295	1259	1250	1176
1161	1155	1102	1014	929	927
913	895	854	834	787	779
755	724	617	518	488	470
437	418	409	382	161	124

ing, such behavior is due to the exponentially increasing number of populated initial levels and is not an artifact of the algorithm.

Conclusion

In this study, we presented two algorithms which may be used to generate the internal energy levels in two different states simultaneously, and which make a description of the temperature de-

pendence of rotovibronic fine structures of electronic transitions as well as rotatory fine structures of vibrational spectra accessible. Both algorithms may readily be extended to consider separable but anharmonic degrees of freedom and to yield the number of levels of a given irreducible representation.

One of the advantages of both algorithms is that only the total intensity of a small fraction of the spectrum must be held in core memory, whereas the complete spectrum is calculated successively. Thus, in case of an unexpected termination of the

TABLE IV.
Number of Generated Transitions at Various Temperatures.

Wave number [cm ⁻¹]	Number of transitions			Wave number [cm ⁻¹]	Number of transitions		
	0 K	60 K	120 K		0 K	60 K	120 K
- 849-- 750	0	0	4	1049-1150	121	2020	49761
- 749-- 650	0	0	16	1149-1250	181	2873	69276
- 649-- 550	0	0	28	1249-1350	286	4087	96145
- 549-- 450	0	0	42	1349-1450	407	5868	133707
- 449-- 350	0	0	84	1449-1550	562	8269	184722
- 349-- 250	0	3	159	1549-1650	789	11474	252504
- 249-- 150	0	8	259	1649-1750	1172	15979	343324
- 149-- 50	0	6	427	1749-1850	1640	22148	466031
- 49-- 50	1	14	624	1849-1950	2250	30456	630336
49-150	1	30	1051	1949-2050	3098	41538	847245
149-250	2	47	1674	2049-2150	4329	56481	1132355
249-350	2	70	2502	2149-2250	5996	76628	1509223
349-450	7	116	3653	2249-2350	8130	103384	2005914
449-550	10	170	5460	2349-2450	10977	138547	2654507
549-650	15	292	8216	2449-2550	14867	184984	3496210
649-750	19	425	12019	2549-2650	20115	246318	4590728
749-850	36	617	17079	2649-2750	26913	326870	6012799
849-950	61	930	24384	2749-2850	35780	431742	7848988
949-1050	86	1394	35086	2849-2950	47532	567930	10207755

TABLE V.
Total CPU Times of the Algorithms at Various Temperatures.

Temperature [K]	Extended algorithm				
	Unmodified desc. freq. ^a	Modified		Interlocked algorithm	
		Asc. freq. ^b	Desc. freq.	Asc. freq.	Desc. freq.
40	5 s	80 s	4 s	72 s	4 s
60	21 s	230 s	12 s	210 s	12 s
80	8960 s	650 s	34 s	600 s	34 s
100	—	1570 s	83 s	1430 s	82 s
120	—	4280 s	230 s	3860 s	220 s
140	—	—	580 s	—	530 s
160	—	—	15920 s	—	1350 s
180	—	—	—	—	2940 s

^aModes in descending frequency order.

^bModes in ascending frequency order.

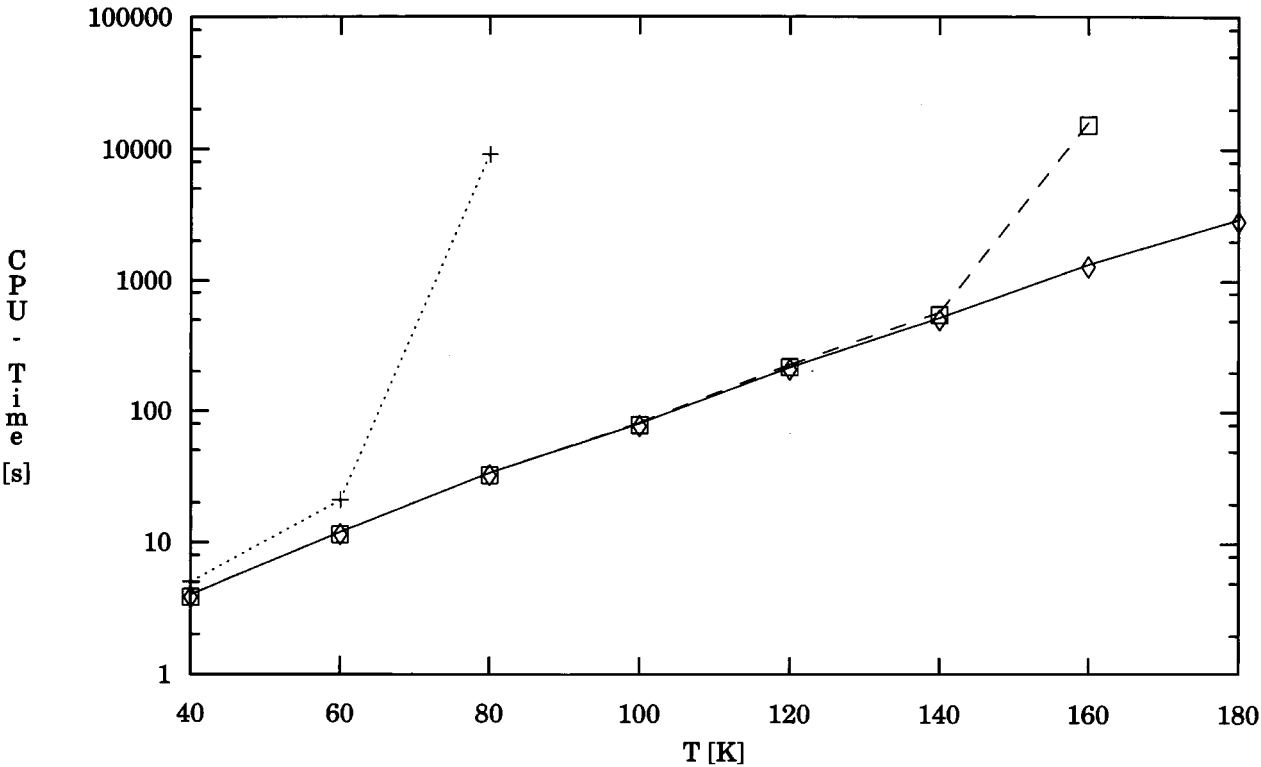


FIGURE 2. CPU times (IBM RS / 6000 590) for various temperatures for the unmodified extended algorithm (dotted line), modified extended algorithm (dashed line), and interlocked algorithm (solid line).

algorithm only the last interval $x_i \pm \Delta x$ has to be recalculated. Because all frequency intervals are obtained individually, parallel computation of the whole spectrum is readily established.

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18. Replace, in step (6) of the extended algorithm, the phrase "start with $k = 2N - 1$ " with "if $V > 0$ and $V > V_{\max}$ start with $k = N - 1$, or else start with $k = 2N - 1$."